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THE ABSORPTION SPECTRA OF NEODYMIUM CHLORIDE AND PRASEODYMIUM CHLORIDE IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL AND MIXTURES OF THESE SOLVENTS.

(With six plates.)

TWENTY-FIRST COMMUNICATION.

BY HARRY C. JONES AND JOHN A. ANDERSON.

(*Read April 25, 1908.*)

(This is a preliminary report on part of an investigation carried out with the aid of a Grant from the Carnegie Institution of Washington.)

The absorption spectra of salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium and erbium have been studied in the present investigation. Of these the salts of neodymium and praseodymium are perhaps the most interesting and important. This is due to the large number of absorption bands shown by these substances, and, further, to the very unusually sharp character of these bands.

The method employed in making the spectrograms consists in allowing light from a spark, or from a Nernst filament, to pass through the solution in question, fall upon a grating and then upon the photographic plate.

For visual work a small direct vision grating pocket spectroscope was found very convenient and useful. For photographing the spectra the vertical grating spectroscope used by Jones and Uhler¹ was employed.

In making the photographs the Seed L-ortho film was used for the region from λ 2000 to about λ 6000.

For photographing the red end of the spectrum a Wratten and Wainwright panchromatic glass plate was used.

¹ Carnegie Publication No. 60.

The Nernst filament was found to be the most satisfactory source of light from the extreme red to the beginning of the ultra-violet. It is sufficiently brilliant to require an exposure of only a minute, but practically ceases at about λ 3200. For wave-lengths shorter than this some spark spectrum must be used.

The cadmium-zinc spark used by Jones and Uhler was fairly satisfactory, especially in the extreme ultra-violet, but has the drawback that there are present a limited number of very intense lines, on a rather faint continuous background. We tried to obtain a spark spectrum having a very large number of lines, but with no lines of very great intensity. We found that tungsten, molybdenum and uranium all satisfied these requirements.

The terminals finally used were prepared by dipping pieces of carbon in a concentrated solution of ammonium molybdate, and then heating in a bunsen burner. They were then dipped into a solution of uranium nitrate and similarly heated.

The coil used to produce the spark was a large Röntgen X-ray coil.

MAKING A SPECTROGRAM.

In making a spectrogram consisting of seven photographic strips, the following mode of procedure was adopted: Seven separate solutions were made up of the desired strengths. The cell² to be used was filled to the required depth with the most concentrated solution of the series, and the quartz plates determining the depth of the solution adjusted to parallelism. The exposure to the Nernst lamp was then made, being usually one minute long. An opaque screen covering up the visible spectrum as far down as λ 4000 was then interposed between the grating and the photographic film, and the exposure to the light of the spark in the ultra-violet made. The duration of this exposure was usually about two minutes. The photographic film was then moved into the proper position for the next exposure. The above series of operations was then repeated for each of the succeeding strips.

After the film had been exposed for each solution and the spark spectrum impressed, it was necessary to make a similar series of

² See Carnegie Publication No. 60.

exposures on a panchromatic plate for the red end of the spectrum, using the same set of solutions.

The scale accompanying the spectrograms was made by photographing an ordinary paper scale. Several photographs were taken, the distance between the paper scale and the lens of the camera being varied slightly from exposure to exposure. The resulting negative which fitted the majority of spectrograms best was selected and used throughout.

NEODYMIUM CHLORIDE IN WATER—BEER'S LAW.

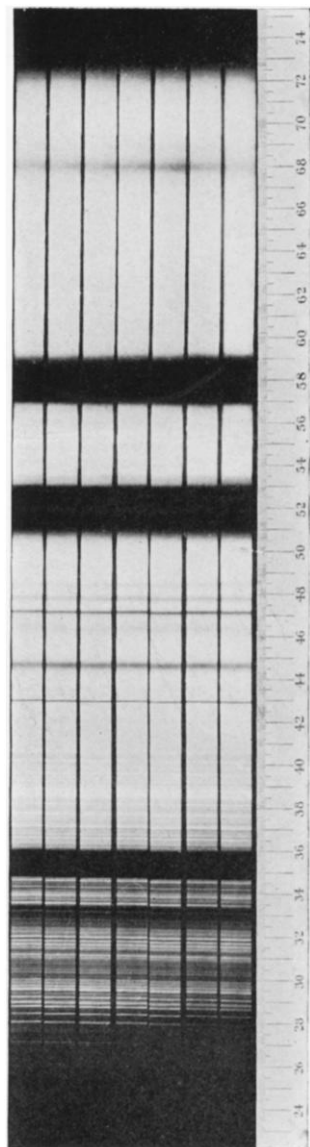
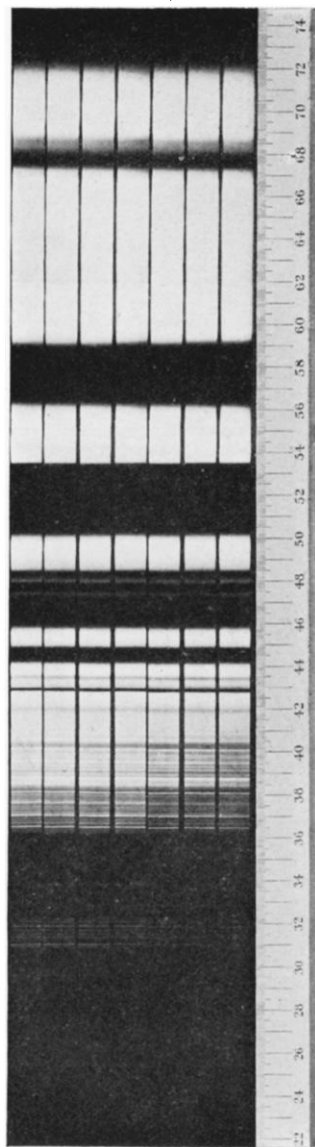
(See plate 1.)

The concentrations of the solutions of neodymium chloride were so chosen and the depths of cell so selected that the total amount of coloring matter in the path of the beam of light was kept constant. From Beer's Law the absorption shown by the several solutions, under these conditions, should be the same. The concentrations of the solutions used in making the negative for *a*, plate 1, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.40, 3.02, 2.72, 2.38, 2.17, 1.90 and 1.70; the corresponding depths of cell being 12, 13.5, 15, 17, 19, 21.5 and 24 mm. For *b*, plate 1, the concentrations were 3.40, 2.55, 1.70, 1.13, 0.80, 0.57 and 0.43; the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18 and 24 mm.

The most concentrated solutions appeared brownish yellow in their bottles, from which the color changed on dilution to a yellowish pink, the color being extremely faint in the most dilute solutions.

The exposures to the light of the Nernst lamp and spark were, respectively, 1 minute and 2 minutes; the slit having a width of 0.01 cm. The exposures and slit width were not varied in the work recorded in the present chapter, the object being to make the spectrograms as nearly comparable as possible.

Both *a* and *b* of plate 1 show the presence of some general absorption in the ultra-violet, which decreases quite rapidly with dilution. The absorption bands also narrow somewhat with decrease in concentration, especially from 3.4 normal to about 1.7 normal. For concentrations less than about 1.5 normal Beer's Law seems to hold very accurately indeed, with the exception of the



shading towards the red accompanying the band near λ 5800, which seems to decrease somewhat with dilution for concentrations of one normal or less.

In the following table the measurements of the positions of the bands were made on the seventh strips of *a*, plate 1, and, therefore, refer to a concentration of 1.7 normal with a depth of layer of 24 mm. The remarks referring to changes with dilution apply to a change in concentration from 3.4 to 1.7 normal, the depths of layer being so varied that the product of concentration and depth remains constant.

λ	Character.	Remarks.
2810	Faint transmission begins.	
2890-2910	Band with well defined sharp edges.	
2970-2995	A double band, strongest component to violet.	The observed narrowing with dilution perhaps due largely to general U. V. absorption.
3220-3330	Strong band of complete absorption, sharp edges.	Narrows slightly with dilution.
3380-3400	Rather faint band, most intense towards red.	
3435-3595	Complete absorption, edges sharp.	
4180	Hazy, not very intense.	Narrows some with dilution.
4275	Very intense and sharp.	Narrows considerably at first.
4290	Narrow and faint.	Between this and λ 4275 is fairly strong absorption in the most concentrated solution. This absorption has disappeared in the spectrum measured.
4330	Hazy.	
4410-4465	Edges rather hazy.	This band is coincident with band due to praseodymium, and is to be ascribed to this element which has not been completely separated from the neodymium. It does not change with dilution.
4580-4650	Band with hazy edges not completely separated from λ 4665- λ 4710.	Narrows slightly with dilution.
4665-4710	More sharply defined on red than on violet side.	Partly due to praseodymium. Does not change with dilution.

λ	Character.	Remarks.
4740-4770	Fairly sharp edges.	Not affected by dilution.
4820	Hazy on violet side.	Due at least partly to praseodymium.
5000-5330	Red limit sharp, violet a little hazy.	Violet shading a little greater in concentrated solutions.
5660-5930	Violet limit sharp. Red edge hazy.	Shading on red side decreases with dilution.
6235	First and strongest band in orange group.	Not affected by dilution.
6260	Narrow and rather faint.	Not affected by dilution.
6270-6310	Faint band.	Not affected by dilution.
6360-6390	Faint band.	Not affected by dilution.
6730	Faint, in shading of principal red band.	Not affected by dilution.
6770-6840	Principal red band. Edges hazy.	Not affected by dilution.
6890	Band with hazy edges.	Not affected by dilution.
7250	End of transmission.	Not affected by dilution.

The most marked change produced by dilution from 3.4 to 1.7 normal, excepting that in the red shading of the λ 5660-5930 band, is that taking place on the red side of the narrow absorption line at λ 4275. In the spectrum of the most concentrated solution the red edge of this line falls at λ 4280, from which place a uniform absorption extends to λ 4295. In the third spectrum, counting from the numbered scale, the shading has almost completely disappeared, leaving a very narrow line at approximately λ 4290. The width of this line is only 2 or 3 A. U. and it persists with unchanged intensity throughout the remaining strips of the spectrogram. Its intensity is, however, not sufficient to make it show in the reproduction, and not even great enough to make it visible on the negative for *b*, plate I.

The limits of transmission for the yellow band, as shown by the spectrum of the most concentrated solution, are λ 5660 and λ 5950; hence the narrowing of its red side amounts to 20 A. U.

b, plate I, starts at the same concentration as *a*, but the effective depth of absorbing layer is only one-fourth of that used in *a*. Hence this spectrogram represents the spectrum of a solution of neodymium chloride 24 mm. deep and having a concentration of 0.43 normal. The absorption bands are all much narrower, and

several of them are shown in the process of breaking up into simpler bands. The bands in the ultra-violet have disappeared excepting the one at λ 3435– λ 3595, which is still intense, and a trace of the one at λ 3220– λ 3330. Transmission in this region now extends faintly to λ 2460. No new absorption bands beyond λ 2800 can be seen.

The λ 3435– λ 3595 band now has the limits λ 3450– λ 3580, and shows a weak transmission at λ 3485, which increases somewhat with dilution, thus dividing the band into two.

The band at λ 4180 is weak throughout *b*, plate 1.

The band having its middle at λ 4445, perhaps due entirely to praseodymium, in *a*, plate 1, has about the same intensity as it shows in a solution of praseodymium chloride having a concentration of 0.85 and a depth of absorbing layer equal to 3 mm. This indicates that the percentage of praseodymium in the neodymium salts used was about 6 per cent. The band at λ 4825 partly due to praseodymium may also be seen throughout the entire series under consideration. The wave-length of the praseodymium band being λ 4815, while that of the band showing in all the neodymium spectra has the position λ 4825, showing that neodymium has a band nearly coincident with that given by praseodymium, but lying a little closer to the red end of the spectrum. The remaining praseodymium band has the position λ 4685, this nearly coinciding with the rather narrow, strong neodymium band whose position is λ 4695.

The band which under *a*, plate 1, was recorded as having the limits λ 4580– λ 4650, shows in *b* as a hazy band with its center at 4615, together with a narrow faint line at λ 4645.

The band which in the table is recorded as λ 4740– λ 4770 has in *b*, plate 1, become a slightly hazy band having its middle at λ 4760. Its intensity is intermediate between that of the bands at λ 4695 and λ 4825.

The band which in *a*, plate 1, has the limits λ 5000– λ 5330, breaks up into a rather complicated series of bands on dilution, some idea of which may perhaps be gained from the following: *b*, plate 1, shows some absorption throughout the region given, but with a deep, narrow band at λ 5090, and faint transmission at λ 5100 and in the region λ 5150– λ 5180. Absorption is complete from λ 5105

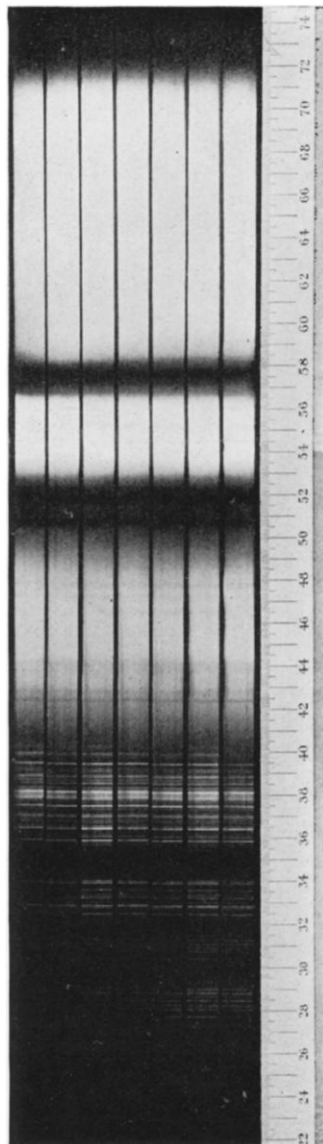
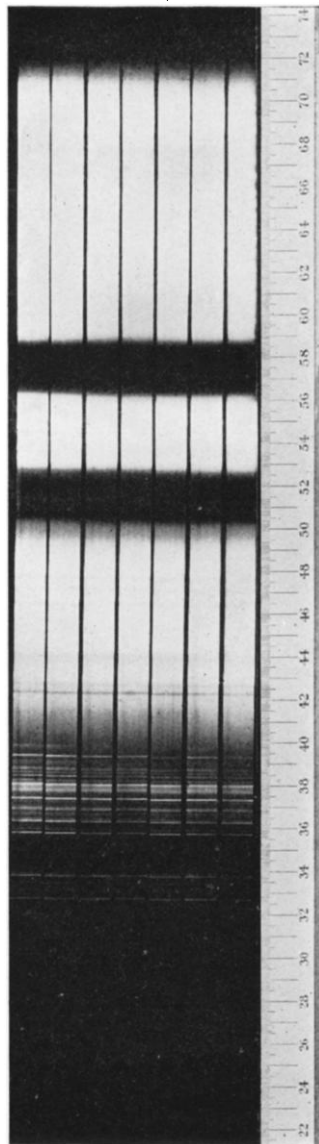
to λ 5150, and from λ 5180 to λ 5270. There is again incomplete absorption from λ 5270 to λ 5330, with indication of a band at λ 5315.

The limits of the yellow band in *b*, plate 1, are λ 5700– λ 5880, in the strip corresponding to the most concentrated solution. The band narrows by 30 Angström units on this spectrogram, the narrowing being due to a decrease in the shading towards the red, with decrease in concentration.

The most intense bands of neodymium chloride, and hence the ones which would be most conspicuous in a very dilute solution are the following: λ 3465, λ 3540, λ 4275, λ 5205, λ 5225, λ 5745, λ 5765 and λ 7325.

The wave-lengths of all the bands are collected in the following table, together with a brief description of the appearance of each band. It is to be understood that this table is not meant to represent what could be seen or photographed in any one solution of neodymium chloride in water. It merely records the positions of all the bands that can be seen in a layer from 3 to 12 mm. deep, when the concentration is varied from 0 to 3.4 normal.

λ	Description.
2900	About 20 A. U. wide.
2985	About 25 A. U. wide.
3225	Narrow and sharp.
3390	Narrow, faint.
3465	Very intense, narrow.
3505	Rather wide.
3540	Very intense, narrow.
3560	Faint, narrow.
4180	Faint, hazy.
4275	Very intense and sharp.
4290	Very narrow, faint.
4330	Hazy edges.
4615	Rather wide and hazy.
4645	Very narrow, faint.
4695	Narrow, intense.
4760	Hazy edges, fairly narrow.
4825	Narrow and fairly intense.
5090	Narrow, intense.
5125	Rather wide and hazy.
5205	Very intense, narrow.
5222	Very intense, narrow.



5255	Narrow, intense.
5315	Hazy edges, faint.
5725	Narrow, intense.
5745	Very intense.
5765	Very intense.
5795	Intense, moderately narrow.
5830	Very faint and hazy.
6235	Fairly narrow.
6260	Very narrow, faint.
6270-6310	Faint, hazy edges.
6360-6390	Faint, hazy edges.
6730	Faint band.
6800	Moderately intense, hazy edges.
6890	Hazy edges.
7325	Very intense and narrow.
7350	Narrow.
7390	Rather wide band.

NEODYMIUM CHLORIDE IN METHYL ALCOHOL—BEER'S LAW.

(See plate 2.)

The concentrations of the solutions used in making the negative for *a*, beginning with the one whose spectrum is adjacent to the numbered scale were 0.50, 0.40, 0.315, 0.25, 0.20, 0.16 and 0.125; the corresponding depths of absorbing layer being 6, 7.5, 9.5, 12, 15, 19 and 24 mm. The concentrations for *b* were in the same order 0.20, 0.16, 0.13, 0.10, 0.08, 0.06 and 0.05, the depths of cell being the same as used in *a*.

There is some absorption in the extreme ultra-violet, which is to be ascribed to the solvent, however, and not to the neodymium chloride.

No trace of absorption due to the dissolved substance is visible until we reach the group of bands near λ 3500. These are three bands having their centers at λ 3475, λ 3505, and λ 3560. Of these the one at λ 3560 is the widest and also the most intense; the one at λ 3475 being somewhat fainter than that at λ 3505. The bands are all much wider and hazier than those occurring near the same place in the aqueous solution. No change with dilution, indicating a deviation from Beer's Law, can be detected in these or any of the other bands in the alcoholic solutions of the chloride.

In the violet and blue regions we find the following band at

λ 4290, about 10 A. U. wide and only moderately intense. At λ 4325 a band somewhat wider and fainter. At λ 4460, a rather wide hazy band with a faint hazy companion towards the violet. This is the band which is perhaps due to praseodymium. The much greater concentration of the alcoholic solutions of praseodymium chloride studied in this work, makes it impossible to verify this by seeing whether the praseodymium band in dilute solution really has this general character.

There are bands at λ 4700, λ 4780 and λ 4825, all of about the same intensity; the one at λ 4770 being, however, much narrower than the other two, of which λ 4825 is somewhat the wider. Both λ 4700 and λ 4780 have faint companions to the violet.

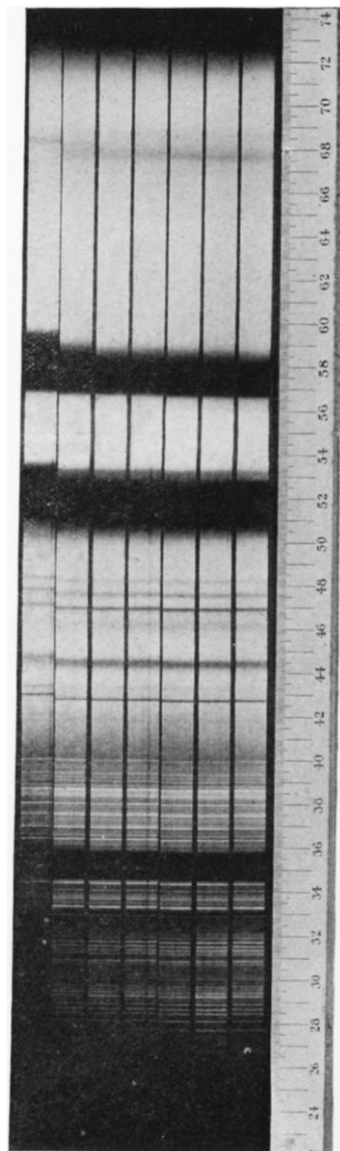
The group in the green is made up of six bands as follows: λ 5125 hazy and rather wide, moderately intense; λ 5180, also hazy but much fainter; λ 5220 moderately intense and narrow; λ 5245 intense and with faint companion towards the red; λ 5290 narrow and moderately intense. Shading as far as λ 5330 with indications of faint band at λ 5315.

The yellow group is made up of seven bands having the following characteristics: λ 5725 moderately intense with hazy edges; λ 5765 narrower, but not quite as intense as λ 5725; λ 5800 fairly narrow, strong; λ 5835 very intense; λ 5860 hazy and moderately intense; not clearly separated from λ 5835 shading to λ 5970, with two faint bands superposed on it, one at λ 5895 and the other at λ 5925.

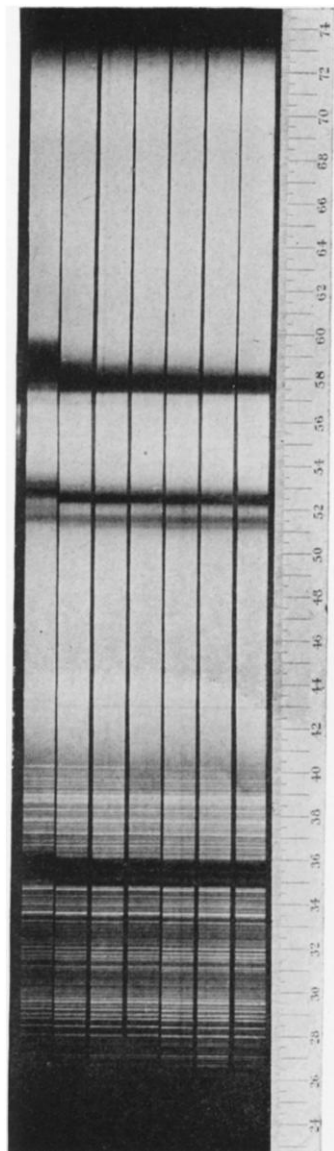
No trace of bands is to be seen in the orange, but in the red there is a fairly narrow but faint band at λ 6860. The spectrum ends at λ 7355 in a deep, rather narrow band. It is evident that the spectrum of neodymium chloride when dissolved in methyl alcohol is quite different from its spectrum in aqueous solution.

NEODYMIUM CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER. (See plates 3 and 4.)

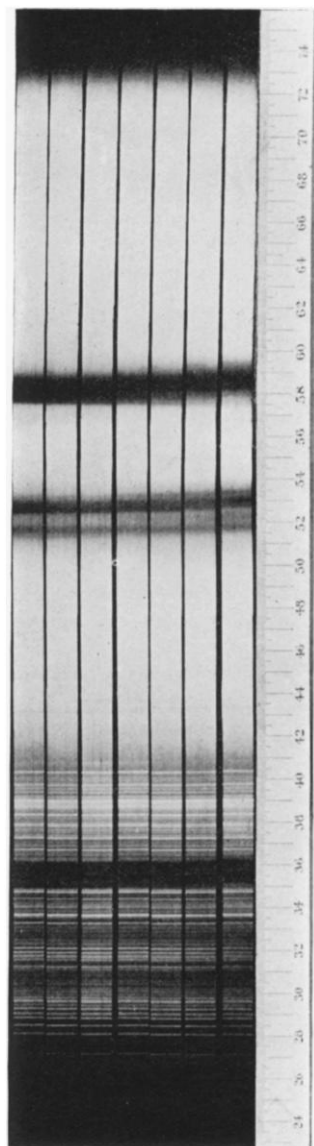
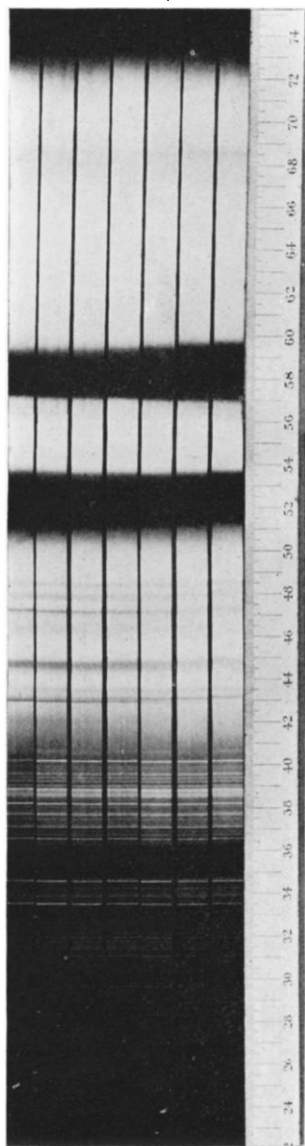
Since, as we have just seen, the absorption spectrum of neodymium chloride in aqueous solution is so different from that of the alcoholic solutions, it was thought to be of some interest to see how the change from one to the other would take place if one of the



A



B



solvents was made to displace the other gradually. A series of solutions was accordingly made up, the concentration of the dissolved salt being constant and equal to 0.5 normal, but the character of the solvent varying as follows: The percentages of water in the seven solutions were 0, 16 $\frac{2}{3}$, 33 $\frac{1}{3}$, 50, 66 $\frac{2}{3}$, 83 $\frac{1}{3}$ and 100; the corresponding percentages of methyl alcohol were 100, 83 $\frac{1}{3}$, 66 $\frac{2}{3}$, 50, 33 $\frac{1}{3}$, 16 $\frac{2}{3}$ and 0. Two spectrograms were made, namely *a*, plate 3, where the depth of the cell was 1.5 cm. and *b* where the cell had a depth of only 5 mm. *a* was made in order to show clearly the change taking place in the narrower and fainter bands, while *b* was intended to show the change of structure of the more intense bands such as the green and yellow ones. The strip which is adjacent to the numbered scale belongs to the solution in pure water, while the one nearest the narrow comparison spark spectrum belongs to the solution in pure methyl alcohol.

Plate 3 shows that beginning with the strip nearest the scale, the first six spectra are very nearly identical. From the sixth to the seventh there is an abrupt change which at first sight consists in a shift of all the bands towards the red, but which on closer examination is seen to consist in a disappearance of one spectrum and the appearance of the other. Since the first strip is the spectrum of the solution in pure water, it follows, since the sixth is nearly identical with the first, that as large a percentage of alcohol in the solvent as 83 per cent. does not change the absorption spectrum materially; the chief change taking place when the percentage of alcohol is varied from 83 per cent. to 100 per cent.

It is to be noted that the apparent shift of the bands towards the red is in reality not quite as great as it appears at first sight from plate 3, owing to the fact that the film accidentally shifted slightly towards the red between the sixth and seventh exposures. The amount of this mechanical shift is easily seen, however, by comparing the spark lines in the ultra-violet. A measurement of the shift shows it to be approximately 3 Angström units, and the same for both *a* and *b*, while the "apparent" shift of the absorption line at $\lambda 4275$ in aqueous solution is actually 15 Angström units, its position in the alcoholic solution being $\lambda 4290$.

The slight changes taking place with some of the bands throughout the spectrograms of plate 3 are perhaps sufficiently clear in the reproductions. However, as a good deal of the detail shown by the negatives is lost even in the most perfect processes of reproduction, we give here a description of the changes taking place in two of the bands as seen on the original negative. We select the bands at $\lambda 4275$, and $\lambda 4760$ from the negative for *a*, plate 3.

In the aqueous solution the $\lambda 4275$ band is very intense and narrow, its whole width being less than 5 Angström units. The edges are only very slightly shaded. In the alcoholic solution the position of the center of the corresponding band is $\lambda 4290$. It has a width of from 12 to 13 Angström units, and is not nearly as intense as in the aqueous solution.

Throughout the first six strips the $\lambda 4275$ band maintains its position and intensity almost unchanged. Its position does not change in the least, but its intensity in the sixth strip is a trifle less than in the others. In the seventh strip there is not the faintest trace left of it. In the third strip, corresponding to the solution whose alcohol content was $33\frac{1}{3}$ per cent., there appears at $\lambda 4285$ an extremely faint and narrow line. In the fourth strip it is somewhat wider and more intense, but its center is still at $\lambda 4285$. In the fifth strip it is beginning to be fairly conspicuous, and in the sixth it is a band of moderate intensity having its center at about $\lambda 4287$. This band is undoubtedly the same one which in the pure alcoholic solution has its center at $\lambda 4290$ or very near there; the exact wavelength being perhaps nearer to $\lambda 4292$. We see then that even when the mixed solvent contains only about one-half alcohol this band exists independent of and distinct from the band characteristic of the aqueous solution; that it is at first only a very narrow and faint line which widens towards the red as the percentage of alcohol is increased.

The band whose center is at $\lambda 4760$ has the following appearance in the aqueous solution: Faint absorption begins at $\lambda 4748$ and rises rapidly to a maximum between $\lambda 4755$ and $\lambda 4760$, then decreases slowly to nothing at $\lambda 4775$. The band is accordingly a trifle asymmetrical, the slope towards the violet being considerably steeper than that towards the red. The corresponding band in the

alcoholic solution is double and answers the following description: Very faint absorption begins at $\lambda 4753$ and rises to a faint maximum at about $\lambda 4757$, becoming again zero at $\lambda 4760$. It begins again at $\lambda 4772$, rises rapidly to a strong maximum at $\lambda 4780$ and falls to zero at $\lambda 4790$. The component whose center is at $\lambda 4757$ is very faint compared with the main band.

In the first and second strips we have nothing but the band corresponding to the aqueous solution. In the third strip the red side of the band has increased slightly in intensity, making it appear much more nearly symmetrical. This change increases in the fourth and fifth strips, the band at the same time widening considerably. In the sixth strip its appearance is as follows: Absorption begins at $\lambda 4748$ and rises to a maximum just to the violet side of $\lambda 4760$, then decreases slightly towards $\lambda 4770$, after which it increases somewhat to $\lambda 4778$, then falls off to zero at $\lambda 4787$.

It is very evident from a study of the change in this band that the two bands characteristic of the aqueous and alcoholic solutions coexist, and that the band appearing in our photographic strips is the sum of the two taken in different proportions. The proportion of the alcohol band being, however, very much smaller than the proportion of alcohol in the corresponding solution. A similar description might be given for any one of the other bands, but this is not necessary as the changes are of exactly the same nature as those we have already indicated. In every case where the alcoholic solution has a strong band, which differs somewhat in position from any band in the aqueous solution, we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent., but the band remains comparatively faint even when the proportion is as high as $83\frac{1}{3}$ per cent.

In order to study the change which takes place between the sixth and seventh strips of the spectrograms of plate 3, more carefully, a series of alcohol solutions were prepared containing the following percentages of water, 0, $2\frac{2}{3}$, $5\frac{1}{3}$, 8, $10\frac{2}{3}$, $13\frac{1}{3}$ and 16. The concentration of the neodymium chloride was constant and equal to 0.5 normal. Two spectrograms were made, one with a depth of absorbing layer of 1.5 cm., in order to show the fainter bands, and the other with the depth of the cell only 5 mm. in order to show as

much as possible of the structure of the larger bands. The first spectrogram is reproduced as *a*, the second as *b*, plate 4. The strips corresponding to the pure alcohol solutions are adjacent to the numbered scale, the spectrum of the solution containing 16 per cent. water being next to the comparison spark spectrum.

Although we found in considering plate 3 that some slight change in the spectrum takes place where the percentage of alcohol is changed from 0 to 83 per cent., yet this change is so small and the bands due to the aqueous solution are so strong that we may regard the spectrum of a solution containing 16 per cent. of water as practically that of the aqueous solution. Accordingly, the spectrograms on plate 4 may be taken to show very nearly the whole change which takes place when the solvent of neodymium chloride is gradually changed from pure water to pure methyl alcohol.

In *a* the ultra-violet band is rather too intense to allow its structure to be seen. Accordingly, we see the whole band remains sensibly unchanged as the water is varied from 16 per cent. to 8 per cent., and then shifts towards the red with increasing rapidity as the water is reduced to zero; the whole apparent shift amounting to about twenty Angström units. On the negative the intense band at λ 3465 may, however, be clearly seen, and its intensity decreases very slowly from the first to the third strips, counting from the narrow comparison spark spectrum. In the fourth strip its intensity is about half of what it was in the first strip, and from this it decreases rapidly, vanishing entirely in the strip nearest the scale. In *b* the structure of this band is seen very distinctly, and we find that the bands characteristic of the aqueous solution gradually decrease in intensity, especially from the third to the sixth strips, while the wider bands characteristic of the alcoholic solutions increase in intensity, the two sets existing together. The change in the band at λ 4275 is the one that shows the best, because here the two bands belonging to the aqueous and alcoholic solutions, respectively, are both intense and narrow and clearly separated from each other. The alcoholic band is clearly visible in the first strip, and it increases continuously in intensity as the amount of water is decreased, but more rapidly from the fourth to the seventh strips than from the first to the fourth. Its position also shifts somewhat

towards the red from the first to the fourth strips, the wave lengths of its center for the two strips being, respectively, λ 4287 and λ 4292. Accompanying this shift is a change in its character which may be gathered from the following statements: In the first strip it has the appearance of an unsymmetrical band, the maximum intensity being nearer the violet; in the third strip it extends from λ 4280 to λ 4295 and has about the same intensity throughout; in the fourth strip the intensity of its violet edge has decreased, while that of the red edge has increased considerably, giving it the appearance of an unsymmetrical band with the maximum intensity towards the red. In the fifth strip the violet shading from λ 4280 to about λ 4284 has disappeared, leaving a band very nearly symmetrical about λ 4290. It appears, therefore, that we are really dealing with two unresolved bands, one having its center at about λ 4285, and the other at λ 4292.

The band at λ 4275, due to the aqueous solution, decreases in intensity throughout, but more rapidly from the third to the sixth strips than at first. Its position remains the same throughout. As near as the eye can judge, this band has had its intensity reduced to about half-value when the fourth strip is reached, corresponding to 8 per cent. of water in the solution. The alcohol band at λ 4292 also has about 50 per cent. of its final intensity in the same solution.

The band at λ 4760 shows the same kind of a change that we described in some detail above, only the change is much more gradual and easy to follow here. It also shows about equal intensity for the two sets of bands when the amount of water is 8 per cent. of the whole.

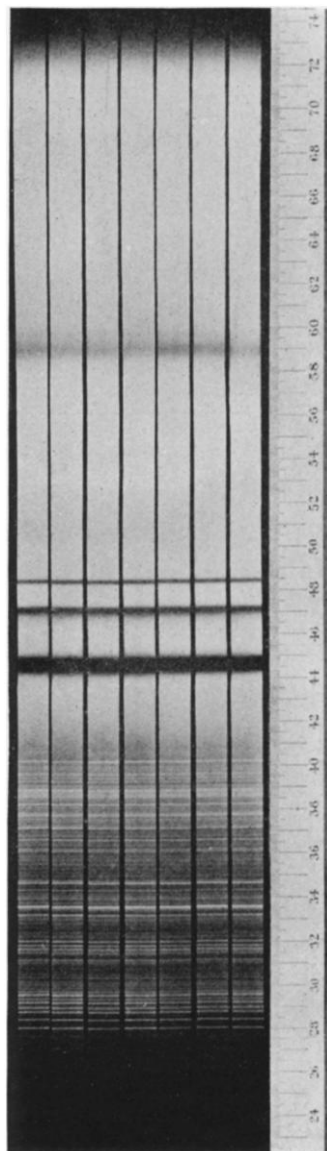
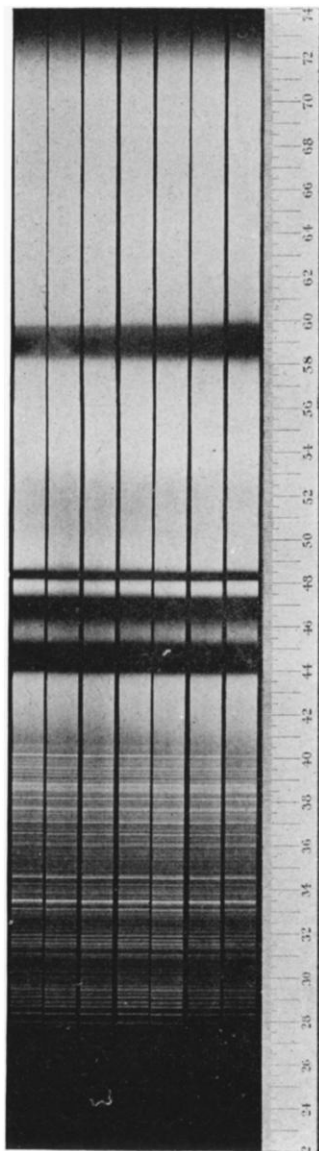
The green and yellow bands are not sufficiently resolved in *a* to allow the change in the individual bands to be followed, and hence these apparently show only a gradual shift towards the red with decrease in the amount of water. In *b*, however, they are sufficiently resolved to enable us to follow the change in each individual band, which, although a little difficult, on account of their large number and the incompleteness of their separation in some cases, may still be done. The change is in every respect the same as we have found for the other bands; namely, those due

to the aqueous solution diminish in intensity and reach about half value in the 8 per cent. aqueous solution, while those belonging to the alcoholic solution increase in intensity, as the amount of water is decreased.

The band in the red near $\lambda 6800$ shows the change very well indeed, the "water" band having the position $\lambda 6800$, while that pertaining to the alcoholic solution is situated at $\lambda 6860$, and hence the two are well separated. Here the point of equal intensity appears to be reached in the solution containing $10\frac{2}{3}$ per cent. of water, but this is due to the fact that the alcoholic band has a considerably greater intensity than that due to the aqueous solution, conditions as to concentration and depth of layer being the same. Taking this into account it is seen that this band obeys substantially the same rule as the others.

The change in the band at $\lambda 7325$ is more difficult to follow, on account of the small intensity of the photographic action on the less refrangible side of this position. The band belonging to the aqueous solution may be seen very clearly even in the strip corresponding to the $2\frac{2}{3}$ per cent. water solution, but is of course entirely absent in the alcoholic solution. Its intensity in the $2\frac{2}{3}$ per cent. solution, however, seems a little greater than we should expect from the behavior of the other bands, but this is perhaps due to the rather weak photographic action in this part of the spectrum, combined with the great intrinsic intensity of the band. The alcoholic solution transmits light as far as $\lambda 7355$ where its spectrum ends abruptly in a band.

Throughout this description we have laid great stress on the fact that on plate 4 the two sets of bands coexist; the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solution increase in intensity with decrease in the percentage of water. We have also called attention to the fact that the two sets of bands have about one-half their full intensity in a solution containing about 8 per cent. of water. This was for a 0.5 normal solution.



PRASEODYMIUM CHLORIDE IN WATER—BEER'S LAW.

(See plate 5.)

The concentrations of the solutions used in making the negative for *a*, beginning with the one whose spectrum is adjacent to the numbered scale were 2.56, 1.92, 1.25, 0.85, 0.60, 0.42 and 0.32. For *b* the concentrations were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14 and 0.11; the depths of absorbing layer being, respectively, 3, 4, 6, 9, 13, 18 and 24 mm.

The solutions of praseodymium chloride are all green or yellowish green, only the intensity of the color changing with change in the concentration.

For these solutions Beer's Law holds very exactly, excepting for the extreme ultra-violet absorption in *a*, and the yellow bands in the two or three most concentrated solutions of *a*.

The limits of transmission in the ultra-violet for the most concentrated and most dilute solutions of *a* are, respectively, λ 2720 and λ 2650. The edge is fairly sharp, indicating the presence of a rather intense band. This is also indicated by *b*, where the spectrum ends abruptly at λ 2630, the limit being the same for all the solutions.

The absorption bands shown in *a* are as follows: λ 4380 to λ 4480, strong band with red edge somewhat shaded; λ 4640 to λ 4710, sharp on red side, quite diffuse towards the violet; λ 4800 to λ 4830, sharply defined on both sides; λ 5860 to λ 5950, both edges diffuse; λ 5985, fairly narrow band with diffuse edges. The region between this band and the principal yellow one shows very strong absorption.

b shows the following: λ 4410 to λ 4465, both edges a little diffuse; λ 4685, fairly narrow band, still more diffuse towards the violet, although somewhat shaded also towards the red; λ 4815, narrow band with edges slightly shaded; λ 5900, wide hazy band; absorption not complete even at its middle; λ 5985, rather faint, hazy band.

The greenish tinge of the solutions would suggest that there is considerable general absorption in the red, because the absorption in the yellow is not sufficient to impart any marked color to the solution, and the bands in the violet and blue could only give it a yellow

tint. The negative for *a* does, in fact, show pretty strong general absorption from λ 7100 to the end of the red, but no doubt a spectrophotometric study of the solutions would show general absorption much farther down into the red. The negative for *b* shows no sign of this absorption for very obvious reasons.

PRASEODYMIUM CHLORIDE IN MIXTURES OF THE ALCOHOLS AND WATER.

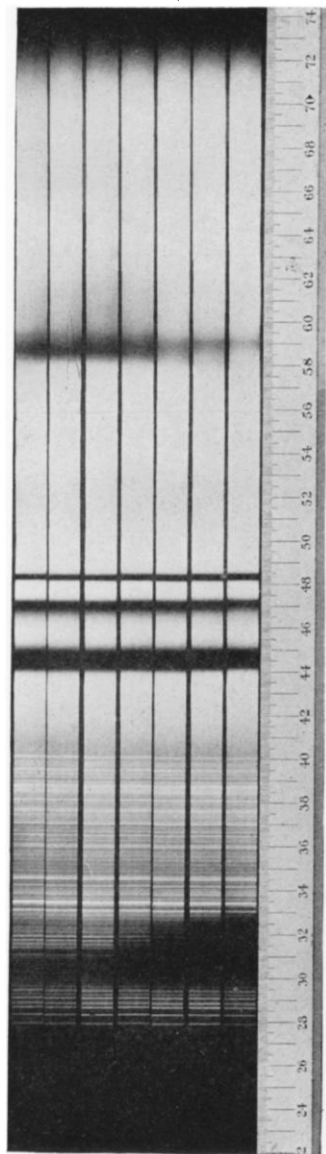
(See plate 6.)

The concentrations of the praseodymium chloride was constant throughout and equal to 0.5 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, $2\frac{1}{3}$, $5\frac{2}{3}$, 8, $10\frac{2}{3}$, $13\frac{1}{3}$ and 16. The depth of absorbing layer was 1.0 cm.

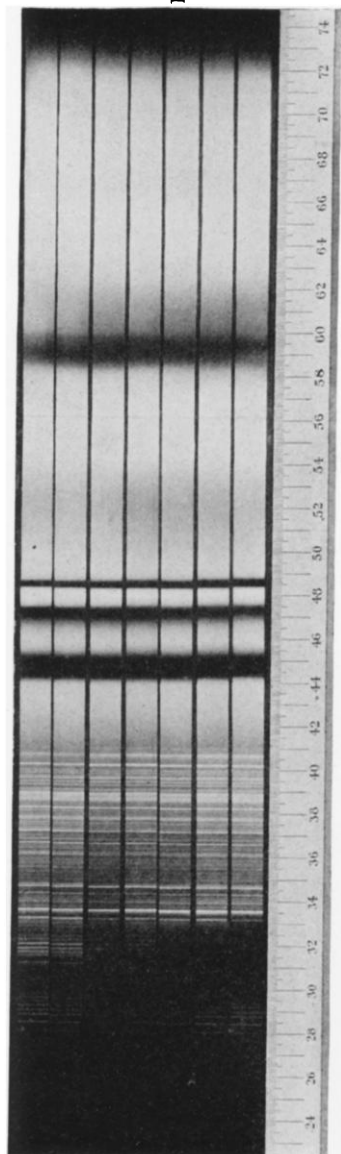
Methyl alcohol was the chief solvent in the solutions pertaining to *a*, while ethyl alcohol was used in the solutions used in making the negative for *b*. The two spectrograms are identical, except for a little greater general absorption in the ultra-violet with the ethyl alcohol.

The most striking feature of the spectrograms is the appearance of the intense absorption band near λ 3000 as the percentage of water is gradually decreased. Only a faint trace of this band is visible with 16 per cent. of water in the solution, and the band is comparatively weak even with only 8 per cent. of water. From this point it increases very rapidly in width and intensity with decrease in the amount of water, until in the pure alcohol solutions its limits (transmission) are λ 2970 and λ 3230, being by far the most intense band in the whole spectrum.

The bands in the violet and blue apparently shift somewhat towards the red, this being, however, due to the fact that the alcohol bands are a little nearer the red end of the spectrum, and that when the percentage of water changes from 16 to 0, the two sets of bands coexist, but are far from being separated. The change is exactly the same in character as the one described in detail in discussing the λ 4760 band in mixtures of alcohol and water for neodymium chloride. The positions of the bands in the solution, containing 16 per cent. of water, are as follows: λ 4390 to λ 4470,



A



B

λ 4660 to λ 4700, λ 4800 to λ 4825. In the solution in pure alcohol they are λ 4410 to λ 4480, λ 4690 to λ 4715, λ 4810 to λ 4840. Hence it appears that the two most refrangible bands have a slightly greater width in the aqueous solution, while the λ 4815 band is more intense in the alcoholic solutions.

The bands in the yellow show very well, indeed; the fact that here as in the spectrum of neodymium chloride we have the coexistence of two sets of bands when the water content of a one-half normal solution is in the neighborhood of 8 per cent. The band in the yellow has already been described under Beer's Law, but as the concentration and depth of layer is different here, the following will serve to indicate what the spectrum of the 16 per cent. aqueous solution shows.

Absorption begins at λ 5850 and rises to a maximum at about λ 5900, then decreases to a minimum at λ 5950, from which it again rises to a maximum at about λ 5980, falling off to zero at λ 6000. The solution in pure alcohol shows the following: Weak absorption begins at λ 5800, and continues without material change up to λ 5880, where it falls almost to nothing. At λ 5900 it begins to increase and reaches a strong maximum at λ 5955, falling off gradually to zero at λ 6000. The intermediate solutions show the gradual disappearance of the bands characteristic of the aqueous solution, and the increase in intensity of those belonging to the alcoholic solution as the percentage of water is gradually decreased. The maximum change takes place from the fifth to the third strips, counting from the numbered scale, indicating here as with neodymium chloride that the two sets have about half their normal intensity when the water content of the solution is about 8 per cent., or when the solution contains about ten molecules of water per molecule of the dissolved substance.

DISCUSSION OF THE RESULTS.

The results established by these plates may be briefly summarized as follows:

1. The absorption spectra of a salt in different solvents are, in general, different.
2. When a salt is dissolved in mixtures of two solvents the

relative percentages of which are varied, there is not a gradual change of one spectrum into the other, but the spectrum given in the mixture is a superposition of the two spectra, the two sets of bands existing together. If the salt is one whose spectrum changes considerably with its state of dissociation, we have in addition to the above phenomena the changes due to the varying dissociation of the dissolved salt produced by the varying composition of the mixture.

A study of all the plates (eighty in number) obtained in this work shows that deviations from Beer's Law is the rule rather than the exception; only a limited number obey Beer's Law even approximately. Beer's Law could only hold in cases where the relative concentrations of the different kinds of absorbers in solution do not change with the dilution, or where the different kinds of absorbers have the same kind of absorption. The first condition is perhaps never realized, while the second is undoubtedly closely approached with such salts as neodymium chloride and praseodymium chloride.

The rule is that the different absorbers have different absorbing powers, and the problem of absorption spectra is to determine which kind of absorbers in solution are responsible for the different bands.

The theory of Ostwald, which would refer absorption in solution mainly to the ions present, has been found to be entirely insufficient to account for the facts established in this investigation.

The other theories which aim to account for the deviations are of two kinds, viz.:

1. Those that assume that the increased absorption in concentrated solutions is due to the formation of aggregates of the molecules of the dissolved substance, or of the molecules and the ions into which they break down in dissociation.

2. Those that assume that the deviation is due to the *formation of solvates*, that is, combinations of the parts of the dissolved substance with the molecules of the solvent.

Now, it has been shown by Hartley and other workers, who have studied the change in the absorption with change in temperature, that the bands which widen with increase in concentration (conditions for Beer's Law assumed to obtain) also widen with

rise in temperature; that is, a rise in temperature produces very much the same effect as increase in concentration. This seems to us pretty conclusive evidence against the theories which are based on the formation of aggregates, for it is well known that the change in the aggregates produced by rise in temperature is *not the same* as that produced by increase in concentration, but *exactly the opposite*.

The theories which assume the formation of solvates are not open to this objection, because it is well known that the change in the solvates produced by rise in temperature is in general the *same* as that produced by increase in concentration. As a solution becomes more concentrated the solvates become simpler and simpler, that is, fewer molecules of the solvent are combined with each part of the dissolved substance. Rise in temperature also breaks down complex solvates into simpler ones. Of course, it does not follow that the solvates of a solution of concentration c_1 at temperature t_1 are *exactly* the same as those in a solution of concentration c_2 at a temperature t_2 ; since under the changed conditions it may happen that the particular solvates, which were most stable when the conditions were c_1 and t_1 , may be less stable than solvates of nearly the same composition at c_2 , t_2 .

For this reason and also because our work on neodymium and praseodymium salts in mixed solvents *seems almost conclusive evidence in favor of the existence of solvates*, we have used the *solvate theory as a working hypothesis throughout this work*. That it is not far from being correct is shown by the fact that all the phenomena observed in the great number, about 1,200, of solutions studied, are accounted for without anything but the simplest assumptions in regard to the behavior of the solvates in question.

The most interesting and important results were obtained from the study of the salts of neodymium and praseodymium, especially those of the former. These substances have not only very many absorption bands, but they are remarkably narrow and sharp, and, hence, peculiarly suitable for spectrographic study. The chief experimental results were the following:

1. The absorption spectrum of aqueous solutions of the chloride and bromide of neodymium changes very little with change in con-

centration, and the two are nearly identical, throughout, excepting for the fact that the absorbing power of the bromide appears to be somewhat greater than that of the chloride.

2. Solutions of the salts in non-aqueous solvents give spectra which are not only different for different salts, but the spectrum of any one salt is different in the different solvents. An apparent exception is the spectrum of neodymium or praseodymium chloride in methyl and ethyl alcohols, which are almost exactly alike.

3. When a salt like neodymium chloride is dissolved in mixtures of water and one of the non-aqueous solvents, and the relative amounts of the two solvents in the mixture is varied, no marked change in the spectrum is observed when the amount of water is changed from 100 per cent. to about 15 or 20 per cent. As the amount of water is still further reduced we find that the solution gives a spectrum which consists of a superposition of the spectra belonging to the aqueous and the non-aqueous solutions; the former decreasing in intensity while the latter increases as the amount of water is decreased. The composition of the mixed solvents, which will show the two spectra with about one-half their normal intensity, depends upon the concentration of the salt in solution; and a constant ratio between the number of molecules of water and those of the dissolved salt were indicated by the experiments, this ratio having the value 10.

Praseodymium chloride, dissolved in mixtures of water and methyl or ethyl alcohol, shows in general the same kind of change in the spectrum as neodymium chloride; but in addition there appears in the alcoholic solutions an entirely new band having no analogue in the aqueous solution. In the former this new band in the ultra-violet is by far the most intense in the entire spectrum. It disappears entirely on addition of water, having about half its normal intensity for a half normal solution when the water content of the solvent is about 8 per cent.

These facts seem to us inexplicable on any other hypothesis than the one we have made, namely, that when a salt of one of these elements is dissolved in any solvent, both *the molecules of the salt and the ions formed from these become solvated, that is, they combine with a certain number of molecules of the solvent.* While in

the case of some salts the spectra point to the existence of solvates of varying complexity, in the case of salts of neodymium and praseodymium they indicate rather the existence of one definite hydrate. A more extended study, including the changes in the spectra produced by changes in temperature, may, however, somewhat modify this conclusion.

Granting the existence of solvates all of the facts observed in connection with the absorption spectra of neodymium and praseodymium salts can be readily explained.

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June, 1908.